

**APPLICATION FOR UNITED STATES
LETTERS PATENT**

**A MATERIAL FOR MAKING HYPER FREQUENCY MULTI-LAYER CHIP
INDUCTORS WITH HIGH PERFORMANCE AND LOW SINTERING TEMPERATURE
AND A PROCESS FOR PREPARING THE MATERIAL**

Inventor(s):

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BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a new material used in manufacturing surface mounting devices and a process of making said material. Particularly, the invention pertains to a material for making high performance hyper frequency multi layer chip inductors, which can be sintered at a low temperature.

2. Description of the Related Art

Multilayer chip inductors ("MLCI"), also known as multilayer ferrite inductors ("MLFI"), are one of the most important surface mounting devices ("SMDS"). The key technical aspect is the co-firing between ferrite and an internal conducting material, such as silver (Ag, chosen for its good conductivity and lower costs). It requires the ferrite to have a low sintering temperature and a high initial permeability. The main materials currently available for manufacturing SMDS are Ni-Zn-Cu ferrite sintered at 850-900 °C and low dielectric constant ceramics. The Ni-Zn-Cu ferrite, has a resonant frequencies below 200 MHz, which may reach 300 MHz if Zn is excluded from the ferrite. Thus, Zi-Zn-Cu ferrite is not suitable for making MLCIs operating in hyper frequencies (300-1000 MHz). On the other hand, low dielectric constant ceramics, with a permeability equal to 1, has been used for making MLCIs operating in ultra high frequencies (> 800 MHz), where high inductance is not required. Therefore, there is no ideal material for making MLCI operating in the frequency region from 300-800 MHz.

In 1950's, Philip developed Co_2Z hexaferrite ($\text{Ba}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$). It generally has a high sintering temperature ($\sim 1300^\circ\text{C}$). Recently, it was found that using a chemical synthetic method with citrate precursor could be used to prepare Co_2Z hexaferrite with a lower formation temperature ($\sim 1150^\circ\text{C}$). The chemical synthetic method also improves compositional homogeneity, which is particularly important for doping elements. However, to the applicants' knowledge, no one has taught or suggested any Co_2Z hexaferrite which can be sintered at a temperature below 900°C .

SUMMARY OF THE INVENTION

The present invention discloses a new material composition used in making high performance hyper frequency multiplayer chip inductors ("hfMLCI") and a process of preparing said composition. The composition of the present invention can be sintered under 900 °C so that the hfMLCI made from this material is suitable for the frequency region of 300-1000 MHz with better inductance and reliability, and can be manufactured with relative lower costs.

The composition of the present invention has a major component and minor component. The major component accounts for 88-99% by weight and the minor component accounts for 1-12% by weight. The major component is Z-type planar hexaferrite having a general formula of $\text{Ba}_3\text{Co}_{2-x-y}\text{Zn}_x\text{Cu}_y\text{Mn}_z\text{Fe}_{24-z-w}\text{O}_{41-3/2(z+w)}$, wherein $0 \leq x \leq 1.0$, $0 \leq y \leq 0.8$, $0 \leq z \leq 1.0$ and $0 \leq w \leq 1.0$. The minor component acts as a sintering aid, having a formulation of $a\text{Bi}_2\text{O}_3 + b\text{V}_2\text{O}_5 + c\text{PbO} + d\text{B}_2\text{O}_3 + e\text{LiF} + f\text{CaF}_2$, where $0 \leq a \leq 1$, $0 \leq b \leq 1$, $0 \leq c \leq 1$, $0 \leq d \leq 1$, $0 \leq e \leq 1$, $0 \leq f \leq 1$.

The composition of the present invention can be prepared by following the steps described below:

(1) weigh out each salt to prepare a solution contain Fe^{3+} , Co^{2+} , Ba^{2+} , Zn^{2+} , Cu^{2+} , Mn^{2+} in predetermined molar ratios, with Fe^{3+} 's concentration being 0.4 - 5 M;

(2) dissolve Fe^{3+} salt in water and add NH_4OH of an equal molar number to precipitate $\text{Fe}(\text{OH})_3$, collect $\text{Fe}(\text{OH})_3$ by filtration and wash it with wa

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The composition of the present invention has a major component and minor component. The major component accounts for 88-99% by weight and the minor component accounts for 1-12% by weight. The major component is Z-type planar hexaferrite having a general formula of $\text{Ba}_3\text{Co}_{2-x-y}\text{Zn}_x\text{Cu}_y\text{Mn}_z\text{Fe}_{24-z-w}\text{O}_{41-3/2(z+w)}$, wherein $0 \leq x \leq 1.0$, $0 \leq y \leq 0.8$, $0 \leq z \leq 1.0$ and $0 \leq w \leq 1.0$. The minor component acts as a sintering aid, having a formulation of $a\text{Bi}_2\text{O}_3 + b\text{V}_2\text{O}_5 + c\text{PbO} + d\text{B}_2\text{O}_3 + e\text{LiF} + f\text{CaF}_2$, where $0 \leq a \leq 1$, $0 \leq b \leq 1$, $0 \leq c \leq 1$, $0 \leq d \leq 1$, $0 \leq e \leq 1$, $0 \leq f \leq 1$.

The composition of the present invention can be prepared by following the steps described below:

(1) weigh out each salt to prepare a solution contain Fe^{3+} , Co^{2+} , Ba^{2+} , Zn^{2+} , Cu^{2+} , Mn^{2+} in predetermined molar ratios, with Fe^{3+} 's concentration being 0.4 - 5 M;

(2) dissolve Fe^{3+} salt in water and add NH_4OH of an equal molar number to precipitate $\text{Fe}(\text{OH})_3$, collect $\text{Fe}(\text{OH})_3$ by filtration and wash it with water, and then dissolve the

freshly prepared $\text{Fe}(\text{OH})_3$ in a citric acid solution (Fe^{3+} /citric acid mole ratio should be 1-2) at 60-80 °C with stirring until the solution becomes transparent;

(3) add all the remaining salts weighed out in step (1), that is, all the salts except Fe^{3+} , to the solution prepared in step (2), add NH_4OH to adjust the pH to 6.0-8.0, and wait for about 2 hours until the solution becomes sol;

(4) incubate the sol obtained in step (3) in an oven at 130-150 °C until it dries up;

(5) heat-treat the dried-up gel at 900-1250 °C for 2-6 hours to obtain Z-type hexaferrite powder;

(6) mix the Z-type hexaferrite powder with the sintering aids, i.e., the minor component of a predetermined formulation, grind the mixture in water or alcohol in a ball mill;

(7) dry up the ground mixture at 80-120 °C, sieved and press into pellets; and

(8) sinter the pellets at 900-1250 °C to obtain the composition of the present invention.

It is also contemplated that the above described procedure can be varied without departing the present invention. For example, although the above procedure stated that Fe^{3+} was first precipitated with NH_4OH before mixing with the other salts weighed out in step (1), it is possible that Fe^{3+} is first mixed all the other salts in a solution and then added with citric acid and NH_4OH , with the resulting solution being used to continue in steps (4)-(8). Another possible variation lies in step (6). While in the above specified procedure the Z-type hexaferrite powder obtained in step (5) is first mixed with the sintering aids before grinding in a ball mill,

it is entirely possible that the Z-type hexaferrite is ground alone and dispersed into ethylene glycol and then mixed with a solution of the sintering aids which, after adjusting the pH, forms a hydroxide coating on the surface of the Z-type hexaferrite particles.

Other objects and features of the present invention will become apparent from the following detailed description considered in conjunction with the accompanying drawings. It is to be understood, however, that the description and drawings are provided solely for purposes of illustration and not as a definition of the limits of the invention, for which reference should be made to the claims.

The various features of novelty which characterize the invention are pointed out with particularity in the claims annexed to and forming a part of the disclosure. For a better understanding of the invention, its operating advantages, and specific objects attained by its use, reference should be had to the drawing and descriptive matter in which there are illustrated and described preferred embodiments of the invention.

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BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings, like reference characters denote similar elements throughout the several views:

Fig. 1 depicts the relationship between the permeability and the frequency for samples 1-1, 1-2, and 1-3 made according to the present invention.

Fig. 2 depicts the relationship between the quality factor and the frequency for samples 1-1, 1-2, and 1-3 made according to the present invention.

Fig. 3 depicts the relationship between the permeability and the frequency for samples 2-1, 2-2, 2-3, 2-4, 2-5, 2-6, 2-7, and 2-8 made according to the present invention.

Fig. 4 depicts the relationship between the quality factor and the frequency for samples 2-1, 2-2, 2-3, 2-4, 2-5, 2-6, 2-7, and 2-8 made according to the present invention.

Fig. 5 depicts the relationship between the permeability and the frequency samples 3-1, 3-2, 3-3, and 3-4 made according to the present invention.

Fig. 6 depicts the relationship between the quality factor and the frequency for samples 3-1, 3-2, 3-3, and 3-4 made according to the present invention.

Fig. 7 depicts the relationship between the permeability and the frequency samples 4-1, 4-2, and 4-3 according to the present invention.

Fig. 8 depicts the relationship between the quality factor and the frequency for samples 4-1, 4-2, and 4-3 made according to the present invention.

Fig. 9 depicts the relationship between the permeability, the quality factor and the frequency for samples 5-1 and 5-2 made according to the present invention.

Fig. 10 depicts the relationship between the permeability, the quality factor and the frequency for samples 6-1 and 6-2 made according to the present invention;

Fig. 11 depicts the relationship between the permeability, the quality factor and the frequency for samples 7-1 and 7-2 made according to the present invention;

Fig. 12 depicts the relationship between the permeability, the quality factor and the frequency for samples 8-1 and 8-2 made according to the present invention;

Fig. 13 depicts the relationship between the permeability, the quality factor and the frequency for samples 9-1 and 9-2 made according to the present invention

Fig. 14 depicts the relationship between the permeability, the quality factor and the frequency for samples 10-1 and 10-2 made according to the present invention.

DETAILED DESCRIPTION OF THE PRESENTLY PREFERRED EMBODIMENTS**Property Measurement**

The magnetic properties were measured using a HP 4291B RF impedance analyzer from 1 MHz to 1800 MHz. The d.c. resistivity at room temperature was measured by HP 4140B using disk sample with silver paste on both sides. The magnetic temperature characteristics were measured at 4 MHz with a HP 4192A LF impedance analyzer at temperatures ranging from -50 °C to 150 °C.

Example 1

In this embodiment, the material composition is to be made from substantially pure Co_2Z hexaferrite as the major component and Bi_2O_3 as the minor component (sintering aid). 96.96 grams of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ are dissolved in water and an appropriate amount of NH_4OH is added to the solution to precipitate $\text{Fe}(\text{OH})_3$. The $\text{Fe}(\text{OH})_3$ precipitate is then dissolved in a solution containing 55 grams of citric acid. Upon the citric acid solution becoming transparent, 5.82 grams of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 7.68 grams of $\text{Ba}(\text{CH}_3\text{COO})_2$ are added. After adjusting the pH to 6-8, the solution becomes a dark-brown sol, which is dried up and calcined at an appropriated temperature to produce dark Co_2Z (Z-type hexaferrite) in formula $\text{Ba}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$ powder 20 grams of the Co_2Z powder and an appropriate amount of Bi_2O_3 are mixed so that the ratio of Co_2Z over Bi_2O_3 is 93:5 by weight. The mixture is ground with iron balls, dried, and pressed into either a disk form or a toroidal form (disks with a outside diameter of 10 mm and a thickness of 1 mm, formed under a pressure of about 2 MPa,

or toroidals with a outside diameter of 20 mm, an inside diameter of 10 mm and a thickness of 3 mm, formed under a pressure of about 7 MPa). The disks or toroidals are sintered at 890 °C (sample 1-1), 920 °C (sample 1-2) or 950 °C (sample 1-3).

Referring to Fig. 1 and Fig. 2, the initial permeability and quality factor over a range of frequencies are shown for samples 1-1, 1-2 and 1-3. Fig. 1 shows that for all the samples the initial permeability is above 4 and the cut-off frequency is above 1800 MHz. Fig. 2 shows that the quality factor at 300 MHz is around 40 for all the samples. The main electric-magnetic properties of the samples are summarized in Table 1, where μ_i is initial permeability, Q is quality factor, $(\alpha_{\mu})_{rel}$ is relative temperature coefficient of inductance, and ρ is insulation resistivity.

Table I

Sample	Condition	μ_i	Q (300 MHz)	$(\alpha_{\mu})_{rel} (/^{\circ}\text{C})$	$\rho (\Omega\cdot\text{cm})$
1-1	890 °C/6h	3.7	40	1.5×10^{-6}	4.4×10^8
1-2	920 °C/6h	3.8	42	9.8×10^{-7}	6.1×10^8
1-3	950 °C/6h	4.6	50	1.7×10^{-6}	5.8×10^8

Example 2

This embodiment is similar to the one described above. The difference lies in the minor component, which is a mixture of compounds, not a single compound as used in Example 1. The minor component in this embodiment comprises Bi_2O_3 , LiF and CaF_2 (1:1:1 by weight). 96.96 grams of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ are dissolved in water and an appropriate amount

of NH_4OH is added to the solution to precipitate $\text{Fe}(\text{OH})_3$. The $\text{Fe}(\text{OH})_3$ precipitate is then dissolved in a solution containing 55 grams of citric acid. Upon the citric acid solution becoming transparent, 5.82 grams of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 7.68 grams of $\text{Ba}(\text{CH}_3\text{COO})_2$ are added. After adjusting the pH to 6-8, the solution becomes a dark-brown sol, which is dried up and calcined at an appropriated temperature to produce dark Co_2Z (Z-type hexaferrite $\text{Ba}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$) powder. 20 grams of the Co_2Z powder and an appropriate amount of the above defined minor component (a complex of Bi_2O_3 , LiF and CaF_2) are mixed so that the weight percentage of the minor component is 1.0 (sample 2-1), 1.5 (sample 2-2), 2.0 (sample 2-3), 2.5 (sample 2-4), 3.0 (sample 2-5), 4.0 (sample 2-6), 6.0 (sample 2-7), or 10.0 (sample 2-8). The mixture is ground with iron balls, dried, and pressed into either a disk form or a toroidal form (disks with a outside diameter of 10 mm and a thickness of 1 mm, formed under a pressure of about 2 MPa, or toroidals with a outside diameter of 20 mm, an inside diameter of 10 mm and a thickness of 3 mm, formed under a pressure of about 7 MPa). The disks or toroidals are sintered at 890 °C.

Referring to Fig. 3 and Fig. 4, the initial permeability and quality factor over a range of frequencies are shown for samples 2-1, 2-2, 2-3, 2-4, 2-5, 2-6, 2-7 and 2-8. Fig. 3 shows that the maximum permeability can be obtained when the minor component accounts for 1.5%. Fig. 4 shows that the quality factor at 300 MHz reaches 40 for all the samples. The main electric-magnetic properties of those samples are summarized in Table 2, where μ_i is initial permeability, Q is quality factor, $(\alpha_\mu)_{\text{rel}}$ is relative temperature coefficient of inductance, and ρ is insulation resistivity.

Table II

Sample	Condition	μ_1	Q (300 MHz)	$(\alpha_{\mu})_{\text{rel}} (/^{\circ}\text{C})$	$\rho (\Omega\cdot\text{cm})$
2-1	890 °C/6h	4.4	50	5.2×10^{-6}	1.9×10^8
2-2	890 °C/6h	4.8	55	1.2×10^{-6}	1.3×10^8
2-3	890 °C/6h	4.5	50	1.6×10^{-6}	2.3×10^8
2-4	890 °C/6h	4.6	52	7.9×10^{-7}	2.8×10^8
2-5	890 °C/6h	4.4	45	1.1×10^{-6}	2.9×10^8
2-6	890 °C/6h	4.0	54	5.8×10^{-7}	2.5×10^8
2-7	890 °C/6h	3.7	50	9.3×10^{-7}	3.2×10^8
2-8	890 °C/6h	3.5	50	1.3×10^{-6}	4.4×10^8

Example 3

This embodiment, as in Example 2, uses a complex minor component comprising Bi_2O_3 , LiF and CaF_2 (ratio is 1=1=1 by weight). 80.41 grams of $\text{FeC}_6\text{H}_5\text{O}_7 \cdot 5\text{H}_2\text{O}$ are dissolved in water. To the solution, 5.82 grams of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 7.68 grams of $\text{Ba}(\text{CH}_3\text{COO})_2$ are added. After adjusting the pH to 6-8 with citric acid and NH_4OH , the solution becomes a dark-brown sol, which is dried up and calcined at an appropriated temperature to produce dark Co_2Z (Z-type hexaferrite in formula $\text{Ba}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$) powder. 20 grams of the Co_2Z powder and an appropriate amount of the above defined minor component (a complex of Bi_2O_3 , LiF and CaF_2) are mixed so that the minor component accounts for 2% by weight. The mixture is ground with iron balls, dried, and pressed into either disks or

toroidals (disks with a outside diameter of 10 mm and a thickness of 1 mm, formed under a pressure of about 2 MPa, or toroidals with a outside diameter of 20 mm, an inside diameter of 10 mm and a thickness of 3 mm, formed under a pressure of about 7 MPa). The disks or toroidals are sintered at 890 °C for 4 hours (sample 3-1), 6 hours (sample 3-2), 8 hours (sample 3-3), or 10 hours (sample 3-4).

Referring to Fig. 5 and Fig. 6, the permeability and quality factor over a range of frequencies are shown for samples 3-1, 3-2, 3-3 and 3-4. It is noted that both the initial permeability and quality factor increases with the duration of sintering incubation. The main electric-magnetic properties of those samples are summarized in Table 3, where μ_i is initial permeability, Q is quality factor, $(\alpha_{\mu})_{rel}$ is relative temperature coefficient of inductance, and ρ is insulation resistivity.

Table III

Sample	Condition	μ_i	Q (300 MHz)	$(\alpha_{\mu})_{rel} (/^{\circ}\text{C})$	$\rho (\Omega \cdot \text{cm})$
3-1	890 °C/4h	4.3	65	8.7×10^{-7}	1.7×10^8
3-2	890 °C/6h	4.8	50	1.2×10^{-6}	2.3×10^8
3-3	890 °C/8h	4.9	50	1.4×10^{-6}	3.8×10^8
3-4	890 °C/10h	5.1	45	2.9×10^{-6}	5.6×10^8

Example 4

The minor component used here is a mixture of B_2O_3 and PbO . 80.41 grams of $FeC_6H_5O_7 \cdot 5H_2O$ dissolved in water. To the solution, 5.82 grams of $Co(NO_3)_2 \cdot 6H_2O$ and 7.68 grams of $Ba(CH_3COO)_2$ are added. After adjusting the pH to 6-8 with citric acid and NH_4OH , the solution becomes a dark-brown sol, which is dried up and calcined at an appropriated temperature to produce dark Co_2Z (Z-type hexaferrite) powder. 20 grams of the Co_2Z powder and an appropriate amount of the above defined minor component (a complex of B_2O_3 and PbO) are mixed so that the minor component's weight accounts for 8% (sample 4-1), 10% (sample 4-2), or 12% (sample 4-3). The mixture is ground with iron balls, dried, and pressed into either disks or toroidals (disks with a outside diameter of 10 mm and a thickness of 1 mm, formed under a pressure of about 2 MPa, or toroidals with a outside diameter of 20 mm, an inside diameter of 10 mm and a thickness of 3 mm, formed under a pressure of about 7 MPa). The disks or toroidals are sintered at 890 °C for 6 hours.

Referring to Fig. 7 and Fig. 8, the permeability and quality factor over a range of frequencies are shown for samples 4-1, 4-2, and 4-3. It is noted that the initial permeability decreases as the percentage of minor component increases. The main electric-magnetic properties of those samples are summarized in Table 4, where μ_i is initial permeability, Q is quality factor, $(\alpha_\mu)_{rel}$ is relative temperature coefficient of inductance, and ρ is insulation resistivity.

Table IV

Sample	Condition	μ_1	Q (300 MHz)	$(\alpha_\mu)_{rel} (/^\circ\text{C})$	$\rho (\Omega\cdot\text{cm})$
4-1	870 °C/6h	3.7	40	2.7×10^{-6}	3.5×10^9
4-1	870 °C/6h	3.4	50	1.1×10^{-6}	2.8×10^9
4-3	870 °C/6h	2.6	50	1.3×10^{-6}	9.6×10^8

Example 5

96.96 grams of $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ are dissolved in water and an appropriate amount of NH_4OH is added to the solution to precipitate $\text{Fe}(\text{OH})_3$. The $\text{Fe}(\text{OH})_3$ precipitate is then dissolved in a solution containing 55 grams of citric acid. Upon the citric acid solution becoming transparent, 3.49 grams of $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, 1.45 grams of $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$, 0.6 grams of $\text{Zn}(\text{NO}_3)_2\cdot \text{H}_2\text{O}$ and 7.68 grams of $\text{Ba}(\text{CH}_3\text{COO})_2$ are added. After adjusting the pH to 6-8, the solution becomes a dark-brown sol, which is dried and calcined to produce black Z-Cu6Zn2 powder in formula $\text{Ba}_3\text{CO}_{2-x-y}\text{Zn}_x\text{Cu}_y\text{Fe}_{24}\text{O}_{41}$, wherein $x=0.2$, $y=0.6$ 20 grams of the Z-Cu6Zn2 powder is dispersed into ethylene glycol and an appropriate amount of $\text{Bi}(\text{NO}_3)_3$ (minor component) added, forming a slurry therein. The minor component should account for 2-4% by weight. The slurry is adjusted to a pH value of 7, dried, and pressed into either a disk form or a toroidal form (disks with a outside diameter of 10 mm and a thickness of 1 mm, formed under a pressure of about 2 MPa, or toroidals with a outside diameter of 20 mm, an inside diameter of 10 mm and a thickness of 3 mm, formed under a pressure of about 7 MPa). The disks or toroidals are sintered at 890 °C (sample 5-1) or 920 °C (sample 5-2) for 6 hours.

The permeability and quality factor over a range of frequencies for samples 5-1 and 5-2 are shown in Fig. 9. The main electric-magnetic properties of those samples are also summarized in Table 5, where μ_i is initial permeability, Q is quality factor, $(\alpha_\mu)_{\text{rel}}$ is relative temperature coefficient of inductance, and ρ is insulation resistivity.

5

Table V

Sample	Condition	μ_i	Q (300 MHz)	$(\alpha_\mu)_{\text{rel}}$ ($1/^\circ\text{C}$)	ρ ($\Omega\cdot\text{cm}$)
5-1	890 $^\circ\text{C}$ /6h	5.3	40	6.7×10^{-7}	1.6×10^8
5-1	920 $^\circ\text{C}$ /6h	6.0	45	8.9×10^{-7}	1.7×10^8

Example 6

96.96 grams of $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ are dissolved in water and an appropriate amount of NH_4OH is added to the solution to precipitate $\text{Fe}(\text{OH})_3$. The $\text{Fe}(\text{OH})_3$ precipitate is then dissolved in a solution containing 55 grams of citric acid. Upon the citric acid solution becoming transparent, 4.07 grams of $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, 1.45 grams of $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$, and 7.68 grams of $\text{Ba}(\text{CH}_3\text{COO})_2$ are added. After adjusting the pH to 6-8, the solution becomes a dark-brown sol, which is dried and calcined to produce black Z-Cu6 powder in formula $\text{Ba}_3\text{CO}_{2-x-y}\text{Zn}_x\text{Cu}_y\text{Fe}_{24}\text{O}_{41}$. 20 grams of the Z-Cu6 powder is dispersed into ethylene glycol and an appropriate amount of $\text{Bi}(\text{NO}_3)_3$ (minor component) added, forming a slurry therein. The minor component should account for 4% by weight. The slurry is adjusted to a pH value of 7, dried, and pressed into either a disk form or a toroidal form (disks with a outside diameter of

10 mm and a thickness of 1 mm, formed under a pressure of about 2 MPa, or toroidals with a outside diameter of 20 mm, an inside diameter of 10 mm and a thickness of 3 mm, formed under a pressure of about 7 MPa). The disks or toroidals are sintered at 890 °C (sample 6-1) or 920 °C (sample 6-2) for 6 hours.

5 The permeability and quality factor over a range of frequencies for samples 6-1 and 6-2 are shown in Fig. 10. The main electric-magnetic properties of those samples are also summarized in Table 6, where μ_i is initial permeability, Q is quality factor, $(\alpha_\mu)_{rel}$ is relative temperature coefficient of inductance, and ρ is insulation resistivity.

10 In this example, the amounts of the precursor compounds can be varied to produce a modified Co_2Z hexaferrite in formula $\text{Ba}_3\text{Co}_{2-x-y}\text{Zn}_x\text{Cu}_y\text{Fe}_{24}\text{O}_{41}$, wherein $X=0.4$ and $y=0.4$ (x and y are defined elsewhere in this disclosure). Using this Co_2Z hexaferrite and follow the same produce described in the preceding paragraphs of this example, disks or toroidals of the same dimentions can be produced and sintered at 890°C (sample 9-2) for 6 hours.

15 The premeability and quality factor over a range of frequencies for samples 9-1 and 9-2 are shown in Fig. 13. The main electric-magnetic properties of those samples are also summarized in Table 9, where μ_i is initial permebility, Q is quality factor, $()_{rel}$ is relative temperature coefficient of inductance, and is insulation resistivity.

20 **Table VI**

Sample	Condition	μ_i	Q (300 MHz)	$(\alpha_\mu)_{rel} (/^\circ\text{C})$	$\rho (\Omega\bullet\text{cm})$
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6-1	890 °C/6h	4.8	40	1.0×10^{-6}	7.8×10^8
6-2	920 °C/6h	5.9	40	2.3×10^{-6}	5.9×10^8

Table IX

Sample	Condition	μ_1	Q (300 MHz)	$(\alpha_\mu)_{rel} (/^\circ\text{C})$	$\rho (\Omega \bullet \text{cm})$
9-1	890 °C/6h	7.7	40	3.3×10^{-6}	6.6×10^{10}
9-2	920 °C/6h	8.3	40	3.4×10^{-6}	9.3×10^{10}

Example 7

80.41 grams of $\text{FeC}_6\text{H}_5\text{O}_7 \cdot 5\text{H}_2\text{O}$ are dissolved in water. To the solution, 5.82 grams of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 7.68 grams of $\text{Ba}(\text{CH}_3\text{COO})_2$ are added. After adjusting the pH to 6-8, the solution becomes a dark-brown sol, which is dried and calcined to produce black Z-type hexaferrite powder. 20 grams of the hexaferrite powder is dispersed into ethylene glycol and an appropriate amount of $\text{Bi}(\text{NO}_3)_3$ (minor component) added, forming a slurry therein.

The minor component should account for 4% by weight. The slurry is adjusted to a pH value of 7, dried, and pressed into either a disk form or a toroidal form (disks with a outside diameter of 10 mm and a thickness of 1 mm, formed under a pressure of about 2 MPa, or toroidals with a outside diameter of 20 mm, an inside diameter of 10 mm and a thickness of 3 mm, formed under a pressure of about 7 MPa). The disks or toroidals are sintered at 890°C (sample 7-1) or 920 °C (sample 7-2) for 6 hours.

The permeability and quality factor over a range of frequencies for samples 7-1 and 7-2 are shown in Fig. 11. The main electric-magnetic properties of those samples are also summarized in Table 7, where μ_i is initial permeability, Q is quality factor, $(\alpha_\mu)_{rel}$ is relative temperature coefficient of inductance, and ρ is insulation resistivity.

5

Table VII

Sample	Condition	μ_i	Q (300 MHz)	$(\alpha_\mu)_{rel} (/^\circ\text{C})$	$\rho (\Omega\cdot\text{cm})$
7-1	890°C/6h	4.4	50	5.4×10^{-7}	6.1×10^8
7-2	920°C/6h	5.2	50	7.1×10^{-7}	9.5×10^8

Example 8

A complex minor component is used in this embodiment, which comprises $\text{Bi}(\text{NO}_3)_3$, $\text{Li}_2(\text{CH}_3\text{COO})$ and $\text{Ca}(\text{NO}_3)_2$ (ratio 1:1:1 by weight). 80.41 grams of $\text{FeC}_6\text{H}_5\text{O}_7 \cdot 5\text{H}_{20}$ are dissolved in water. To the solution, 3.49 grams of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 1.45 grams of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 0.6 grams of $\text{Zn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ and 7.68 grams of $\text{Ba}(\text{CH}_3\text{COO})_2$ are added. After adjusting the pH to 6-8, the solution becomes a dark-brown jelly, which is dried and calcined to produce black Z-Cu₆Zn₂ powder in formula $\text{Ba}_3\text{CO}_{2-x-y} \text{Zn}_x\text{Cu}_y\text{Fe}_{24}\text{O}_{41}$, wherein $x=0.2$ and $y=0.6$. 20 grams of the hexaferrite powder is dispersed into ethylene glycol and an appropriate amount of the above-specified minor component is added, forming a slurry therein. The minor component should account for 3% by weight. The slurry is adjusted to a pH value of 7, dried, and pressed into either a disk form or a toroidal form (disks with a outside

diameter of 10 mm and a thickness of 1 mm, formed under a pressure of about 2 MPa, or toroidals with a outside diameter of 20 mm, an inside diameter of 10 mm and a thickness of 3 mm, formed under a pressure of about 7 MPa). The disks or toroidals are sintered at 890 °C (sample 8-1) or 920 °C (sample 8-2) for 6 hours.

5 The permeability and quality factor over a range of frequencies for samples 7-1 and 7-2 are shown in Fig. 12. The main electric-magnetic properties of those samples are also summarized in Table 8, where μ_i is initial permeability, Q is quality factor, $(\alpha_\mu)_{rel}$ is relative temperature coefficient of inductance, and ρ is insulation resistivity.

10 **Table VIII**

Sample	Condition	μ_i	Q (300 MHz)	$(\alpha_\mu)_{rel} (/^\circ\text{C})$	$\rho (\Omega\cdot\text{cm})$
8-1	890 °C/6h	4.3	50	2.7×10^{-6}	3.5×10^8
8-2	920 °C/6h	4.8	45	1.5×10^{-6}	5.2×10^8

Example 9

In this embodiment, Z-Mn2 hexaferrite in formula $\text{Ba}_3\text{CO}_{2-x-y} \text{Zn}_x\text{Cu}_y\text{Fe}_{24}\text{O}_{41}$, (wherein $Z=0.2$, $W=0.8$) is the major component. The minor component comprises Bi_2O_3 and V_2O_5 (ratio of 1:1 by weight). 92.2 grams of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ are dissolved in water and an appropriate amount of NH_4OH is added to precipitate $\text{Fe}(\text{OH})_3$. The $\text{Fe}(\text{OH})_3$ precipitate is then dissolved in a solution containing 55 grams of citric acid. Upon the citric acid solution becoming transparent, 5.82 grams of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 7.68 grams of $\text{Ba}(\text{CH}_3\text{COO})_2$ and

0.358 gram of $\text{Mn}(\text{NO}_3)_2$ are added. After adjusting the pH to 6-8, the solution becomes a dark-brown sol, which is dried and calcined at an appropriated temperature to produce dark Z-Mn₂ hexaferrite powder, 20 grams of the powder and an appropriate amount of the above defined minor component are mixed so that the weight percentage of the minor component is 2.0%. The mixture is ground, dried and pressed into either disks or torodials (disk with an outside diameter of 10 mm and a thickness of 1 mm, formed under a pressure of about 2Mpa, or torodials with an outside diameter of 20mm, an inside diameter of 10mm and a thickness of 3mm, formed under a pressure of about 7Mpa). The disks or torodials are sintered at 870 °C (sample 10-1), 890 °C (sample 10-2) and 920 °C (sample 10-3).

The foregoing examples demonstrate that the new material prepared according to the present invention using lower sintering temperatures represents significant improvement in sintering behavior, homogeneity of grain size, density, initial permeability, quality factor, insulation resistivity and natural ferromagnetic resonance at frequencies over 1.0 GHz. Therefore, it process a great potential as a soft magnetic material for manufacturing hfMLCIs.

Figure 14 shows the permeability and quality factor over a range of frequencies for samples 10-1, 10-2 and 10-3. For all the samples the initial permeability is above 4 and the quality factor at 300 MHz is above 60. The main electric-magnetic properties of the samples are also summarized in table 10, where μ_i is the initial permeability, Q is quality factor, $(\alpha_\mu)_{\text{rel}}$ is relative temperature coefficient of inductance, and ρ is insulation resistivity

Table X

Sample	Condition	μ_i	Q (300 MHz)	$(\alpha_{\mu})_{rel} (/^{\circ}\text{C})$	$\rho (\Omega\cdot\text{cm})$
10-1	890 °C/6h	4.2	80	2.5×10^{-6}	7.8×10^8
10-2	920 °C/6h	4.3	90	1.8×10^{-6}	9.5×10^8
10-3	950 °C/6h	4.7	60	1.7×10^{-6}	1.2×10^9

The foregoing examples demonstrate that the new material prepared according to the present invention using lower sintering temperatures represents significant improvement in sintering behavior, homogeneity of grain size, density, initial permeability, quality factor, insulation resistivity and natural ferromagnetic resonance at frequencies over 1.0 GHz. Therefore, it process a great potential as a soft magnetic material for manufacturing hfMLCIs.

Thus, while there have shown and described and pointed out fundamental novel features of the invention as applied to a preferred embodiment thereof, it will be understood that various omissions and substitutions and changes in the form and details of the devices illustrated, and in their operation, may be made by those skilled in the art without departing from the spirit of the invention. For example, it is expressly intended that all combinations of those elements and/or method steps which perform substantially the same function in substantially the same way to achieve the same results are within the scope of the invention. Moreover, it should be recognized that structures and/or elements and/or method steps shown and/or described in connection with any disclosed form or embodiment of the invention may be incorporated in any other disclosed or described or suggested form or embodiment as a general

matter of design choice. It is the intention, therefore, to be limited only as indicated by the scope of the claims appended hereto.

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